Standard Operating Procedure for the Determination of Extractable Petroleum Hydrocarbons (based on MADEP EPH)

1.0 Scope and Application:

This method is designed to measure the collective concentrations of extractable aliphatic and aromatic petroleum hydrocarbons in water and soil/sediment matrices. Extractable aliphatic hydrocarbons are collectively quantitated within two ranges: C9 through C18 and C19 through C36. Extractable aromatic hydrocarbons are collectively quantitated within the C11 through C22 range.

1.2 This method is based on a solvent extraction, silica gel solid-phase extraction (SPE)/fractionation process, and gas chromatography (GC) analysis using a flame ionization detector (FID). This procedure should be used by, or under the supervision of, analysts experienced in extractable organics analysis. Analysts should be skilled in the interpretation of gas chromatograms and their use as a quantitative tool.

1.3 This method was designed by the Massachusetts Department of Environmental Protection (MADEP) to evaluate human health hazards that may result from exposure to petroleum hydrocarbons. It is intended to produce data in a format suitable for evaluation by that approach and that may be compared to reporting and cleanup standards.

1.4 The fractionation step described in this method can be eliminated to allow for a determination of a Total Petroleum Hydrocarbon (TPH), and/or to obtain qualitative “fingerprinting” information. While TPH provides little information on the chemical constituents, toxicity, or environmental fate of petroleum mixtures, it may be a cost-effective screening tool in cases where relatively low concentrations of contamination are suspected.

1.5 Petroleum products suitable for evaluation by this method include kerosene, fuel oil #2, fuel oil #4, fuel oil #6, diesel fuel, jet fuel, and certain lubricating oils. This method, in and of itself, is not suitable for the evaluation of gasoline, mineral spirits, petroleum naphthas, or other petroleum products which contain a significant percentage of hydrocarbons lighter than C9. This method, in and of itself, is also not suitable for the evaluation of petroleum products which contain a significant percentage of hydrocarbons heavier than C36.

1.6 This method includes a data adjustment step to subtract the concentration of Target PAH Analytes from the concentration of C11 through C22 Aromatic Hydrocarbons. This data adjustment may be made by the laboratory or the data user.

1.7 Data reports produced using this method must contain all of the required EPH/TPH data information provided in Appendix 3. The format of these data reports is left to the discretion of individual laboratories.

1.8 Like all GC procedures, this method is subject to a "false positive" bias in the reporting of Target PAH Analytes, in that non-targeted hydrocarbon compounds eluting or co-eluting within a specified retention time window may be falsely identified and/or quantified as a Target or Diesel PAH Analyte. More detail concerning the applicability of the method and the subjective nature to false positives can be found in the original method (see references).

2.0 Minimum Detection Limit (MDL) & Minimum Reporting Limit (MRL):

2.1 The Reporting Limit (RL) of this method for each of the collective aliphatic and aromatic fractional ranges is approximately **20 mg/kg** in soil/sediment, and approximately **100 μg/L** in water. The RL of this method for TPH is approximately **10 mg/kg** in soil and approximately **100 μg/L** in water. The RL of this method for the Target PAH Analytes is compound-specific, and ranges from approximately 0.2 to 1.0 mg/kg in soil/sediment, and 2 to 5 μg/L in water. The detection limits studies are performed during every 12 months, they are statistical values based on the EPA's procedure to determine Detection Limits and were calculated from actual analysis on BEL's Gas Chromatographic system during a span of 3 days. The matrix was prepared in the laboratory with interference free reagents and materials.

2.2 MDL determinations are repeated annually in reagent water matrix.

2.3 This method is suitable for the analysis of waters, soils, sediments, wastes, sludge's, and non-aqueous phase liquids (NAPL). However, it should be noted that the method was validated only for soil and water matrices.

2.4 This method is based on (1) USEPA Methods 8000B, 8100, 3510C, 3520C, 3540C, 3541, 3545A, 3546, 3580 A and 3630C, SW-846, "Test Methods for Evaluating Solid Waste"; (2) Draft "Method for Determination of Diesel Range Organics", EPA UST Workgroup, November, 1990; and (3) "Method

for Determining Diesel Range Organics", Wisconsin Department of Natural Resources, PUBL-SW-141, 1992.

3.0 METHOD SUMMARY

3.1 A sample submitted for EPH analysis is extracted with methylene chloride, dried over sodium sulfate, solvent exchanged into hexane, and concentrated in a Kuderna-Danish Type of solvent concentrating apparatus. Sample cleanup and separation into aliphatic and aromatic fractions is accomplished using commercially available silica gel cartridges or prepared silica gel columns. The two individual fraction extracts produced are re-concentrated to a final volume of 1 mL (i.e., an aliphatic extract and an aromatic extract). The concentrated extracts are then separately analyzed by a capillary column gas chromatograph equipped with a flame ionization detector. The resultant chromatogram of aliphatic compounds is collectively integrated within the C9 through C18 and C19 through C36 ranges. The resultant chromatogram of aromatic compounds is collectively integrated within the C11 through C22 range, and is (optionally) used to identify and quantitated individual concentrations of Target PAH Analytes.

3.2 Average calibration factors or response factors determined using an aliphatic hydrocarbon standard mixture are used to calculate the collective concentrations of C9 through C18 and C19 through C36 aliphatic hydrocarbons. An average calibration factor or response factor determined using a PAH standard mixture is used to calculate a collective C11 through C22 aromatic hydrocarbon concentration. Calibration factors or response factors determined for individual components of the PAH standard mixture are also used to calculate individual concentrations of Target PAH Analytes.

4.0 DEFINITIONS

4.1 Internal Standard (IS) -- A pure analyte(s) added to a sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same sample or solution. The internal standard must be an analyte that is not a target component nor should it be in the sample.

4.2 Surrogate Analyte (SA) -- A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added directly to a sample aliquot in known amount(s) before extraction or other processing and is measured with the same procedures used to measure

other sample components. The purpose of a surrogate analyte is to monitor method performance with each sample.

4.3 Laboratory Duplicates (LD1 and LD2) -- Two sample aliquots, taken in the laboratory from a single sample bottle, and analyzed separately with identical procedures. Analysis of LD1 and LD2 indicate precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures. This method cannot utilize laboratory duplicates since sample extraction must occur in the sample vial and sample transfer is not possible due to analyte volatility.

4.4 Field Duplicates (FD1 and FD2) -- Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analysis of FD1 and FD2 give a measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures. Since laboratory duplicates cannot be analyzed, the collection and analysis of field duplicates for this method is critical.

4.5 Laboratory Reagent Blank (LRB) -- An aliquot of reagent water, or other blank matrix, that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

4.6 Field Reagent Blank (FRB) -- Reagent water, or other blank matrix, that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to sampling site, exposure to sampling site conditions, storage, preservation and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

4.7 Laboratory Fortified Blank (LFB) -- An aliquot of reagent water, or other blank matrix, to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise analyte quantitation at various concentrations including the required method detection limit.

4.8 Laboratory Fortified Sample Matrix (LFM) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

4.9 Stock Standard Solution (SSS) -- A concentrated solution containing one or more method analytes which is typically purchased from reputable certified suppliers using

assayed reference materials, the certificate rec'd with the mix must be kept on file for reference. Note: One stock standard solution mix need not contain all the target analytes.

4.10 Primary Dilution Standard Solution (PDS) -- A solution of several analytes prepared in the laboratory from commercial stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

4.11 Calibration Standard (CAL) -- A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standard(s) and surrogate analyte(s). The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

4.12 Quality Control Sample (QCS) -- A solution of method analytes which is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source **external** to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials, sometimes called the **second source**.

4.13 Laboratory Performance Check Solution (LPC) -- A solution of selected method analytes, surrogate(s), internal standard(s), or other test substances used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

4.14 Method Detection Limit (MDL) -- The minimum concentration of an analyte that can be identified measured and reported with 99% confidence that the analyte concentration is greater than zero. (Appendix B to 40 CFR Part 136)

4.15 Estimated Detection Limit (EDL) -- Defined as either the MDL or a level of compound in a sample yielding a peak in the final extract with a signal to noise (S/N) ratio of approximately five, whichever is greater.

4.16 Procedural Standard Calibration -- A calibration method where aqueous calibration standards are prepared and processed (e.g., purged, extracted, and/or derivatized) in exactly the same manner as a sample. All steps in the process from addition of sampling preservatives through instrumental analysis are included in the calibration. Using procedural standard calibration compensates for any inefficiency in the processing procedure.

4.17 Aliphatic Hydrocarbon Standard is defined as a 14 component mixture of the normal alkanes listed in Table 1. The compounds comprising the Aliphatic Hydrocarbon Standard are used to (a) define and establish windows for the two aliphatic hydrocarbons ranges, and (b) determine average calibration or response factors that can in turn be used to calculate the collective concentration of aliphatic hydrocarbons in environmental samples within those hydrocarbon ranges.

4.18 **Analytical Batch** is defined as a group of field samples with similar matrices which are processed as a unit. For Quality Control purposes, if the number of samples in such a group is greater than 20, then each group of 20 samples or less is defined as a separate analytical batch.

4.19 **Aromatic Hydrocarbon Standard** is defined as a 17 component mixture of the polynuclear aromatic hydrocarbons (PAHs) listed in Table 2. The compounds comprising the Aromatic Hydrocarbon Standard are used to (a) define the individual retention times and calibration or response factors for each of the PAH analytes listed in Table 2, (b) define and establish the window for the C11 through C22 Aromatic Hydrocarbon range, and (c) determine an average calibration or response factor that can in turn be used to calculate the collective concentration of aromatic hydrocarbons in environmental samples within the C11 through C22 hydrocarbon range.

4.20 **C9 through C18 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbon compounds which contain between nine and 18 carbon atoms and are associated with the release of a petroleum product to the environment. In the EPH method, C9 through C18 aliphatic hydrocarbons are defined and quantitated as compounds which elute from n-nonane (C9) to just before n- nonadecane (C19).

Table 1.
Aliphatic Hydrocarbon Standard

Carbon Number	Compound	**Retention Time* (min)**
9	n-Nonane	**3.2**
10	n-Decane	**4.6**
12	n-Dodecane	**7.9**
14	n-Tetradecane	**11.1**
16	n-Hexadecane	**14.1**
18	n-Octadecane	**16.7**
19	n-Nonadecane	**18.0**
20	n-Eicosane	**19.1**

1-chlorooctadecane	Surrogate	**20.1**
5-alphaandrostane	Internal Standard	**21.3**
22	n-Docosane	**21.4**
24	n-Tetracosane	**23.4**
26	n-Hexacosane	**25.3**
28	n-Octacosane	**27.0**
30	n-Triacontane	**28.7**
36	n-Hexatriacontane	**34.8**

*** Value herein presented is aproximate**

Table 2
Poly Aromatic Hydrocarbonds

PAH Compound	RT (aprox min)	MDL Water (ug/L)	MDL Soil (ug/kg)
Naphthalene	7.66	0.14	0.09
2-Methylnaphthalene	9.49	0.18	0.09
Acenaphthylene	11.93	0.14	0.09
Acenaphthene	12.46	0.16	0.09
Fluorene	13.89	0.25	0.09
Phenanthrene	16.54	0.31	0.16
Anthracene	16.66	0.30	0.16
Ortho-Terphenyl (surr)	17.95	0.31	0.13
Fluoranthene	19.92	0.47	0.16
Pyrene	20.51	0.47	0.16
Benzo(a)Anthracene	24.08	0.60	0.19
Chrysene	24.21	0.60	0.19
Benzo(b)Fluoranthene	26.94	0.60	0.19
Benzo(k)Fluoranthene	27.02	0.66	0.16
Benzo(a)Pyrene	27.66	0.50	0.16
Indeno(1,2,3-cd)Pyrene*	30.25	0.41	0.13
(a,h)Anthracene*	30.36	0.44	0.13
Benzo(g,h,i)Perylene	30.76	0.57	0.13

* Indeno(1,2,3-cd)Pyrene and Dibenzo(a,h)anthracene may co-elute under the column and chromatographic conditions described herein.

4.21 C19 through C36 Aliphatic Hydrocarbons are defined as all aliphatic hydrocarbon compounds which contain between 19 and 36 carbon atoms and are associated with the release of a petroleum product to the environment. In the EPH method, C19 through C36 aliphatic hydrocarbons are de-

fined and quantitated as compounds, which elute from n-nonadecane (C19) to just after hexatriacontane (C36).

4.22 **C11 through C22 Aromatic Hydrocarbons** are defined as all aromatic hydrocarbon compounds which contain between 11 and 22 carbon atoms and are associated with the release of a petroleum product to the environment. In the EPH method, C11 through C22 aromatic hydrocarbons are defined and quantitated as compounds which elute from naphthalene to just after benzo(g,h,i)perylene, excluding Target PAH Analytes.

4.23 Diesel PAH Analytes are defined as naphthalene, 2-methylnaphthalene, phenanthrene, and acenaphthene, and are a subset of Target PAH Analytes. For most sites known to be contaminated by a release of diesel and/or #2 fuel oil only, Diesel PAH Analytes will be the only Target PAH Analytes of interest.

4.24 Extractable Petroleum Hydrocarbons (EPH) are defined as collective fractions of hydrocarbon compounds eluting from n-nonane to n-hexatriacontane, excluding Target PAH Analytes. EPH is comprised of C9 through C18 Aliphatic Hydrocarbons, C19 through C36 Aliphatic Hydrocarbons, and C11 through C22
Aromatic Hydrocarbons.

4.25 Fractionation Surrogate Standards are compounds that are added to sample extracts immediately prior to fractionation at known concentrations to evaluate fractionation efficiency.

4.26 Total Petroleum Hydrocarbons (TPH) are defined as the collective concentration of all hydrocarbon compounds eluting from n-nonane to n-hexatriacontane, **excluding Target PAH Analytes**. TPH is equivalent to the summation of C9 through C18 Aliphatic Hydrocarbons, C19 through C36 Aliphatic Hydrocarbons, and C11 through C22 Aromatic Hydrocarbons.

4.27 Unadjusted C11 through C22 Aromatic Hydrocarbons are defined as all aromatic hydrocarbon compounds eluting from naphthalene through benzo(g,h,i)perylene.

4.28 **Unadjusted TPH** is defined as the collective concentration of all hydrocarbon compounds eluting from nnonane to n-hexatriacontane, **including the Target PAH Analytes**.

5.0 INTERFERENCES AND CONTAMINATION

5.1 Impurities contained in the extraction solvent usually account for the majority of the analytical problems. Each new bottle of solvent should be analyzed for interferences before use. An interference free solvent is a solvent containing no peaks yielding data above the MDL (Appendix A) at the retention times of the analytes of interest (target analyte). Indirectly, daily checks on the extracting solvent are obtained by monitoring the laboratory reagent blanks (Section 9.3). Whenever interference is noted in the reagent blank, the analyst should analyze the solvent separately to determine if the source of the problem is the solvent or another reagent.

5.2 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by thoroughly rinsing with the last solvent used in it. Follow by washing with hot water and detergent and thoroughly rinsing with tap and reagent water. Drain dry, and heat in an oven or muffle furnace at 200°C for one hour. **Do not muffle volumetric ware** but instead rinse three times with HPLC grade or better acetone. Thoroughly rinsing all glassware with HPLC grade or better acetone may be substituted for heating provided method blank analysis confirms no background interfering contamination is present. After drying and cooling, seal and store all glassware in a clean environment free of all potential contamination. To prevent any accumulation of dust or other contaminants, store glassware inverted on clean aluminum foil or capped with aluminum foil.

5.3 Commercial lots of the extraction solvents (Methylene Chloride and n-Hexane) often contain observable amounts of solvent impurities, testing a solvent blank will help discover this. When present, these impurities can normally be removed by double distillation.

5.4 Interfering and erratic peaks have been observed in method blanks these may be due to phthalate contamination. This contamination can be reduced by paying special attention to reagent preparation and elimination of all forms of plastic from the procedure (i.e., HDPE bottles, plastic weighing boats, etc.).

5.5 Cross-contamination can occur whenever a low- concentration sample is analyzed immediately after a high concentration sample. To reduce carryover, the sample syringe must be rinsed between samples with solvent. Whenever an unusually concentrated sample is encountered, it must be followed by the analysis of a system solvent blank to check for cross-contamination. However, due to the potential for samples to be analyzed using an auto-sampler, the ability to perform this blank analysis may not always be possible. If the sample analyzed immediately after the unusually concentrated sample is free from contamination, then the assumption can be made that carryover or cross-contamination is not an issue. However, if this sample did detect analytes which were present in the unusually concentrated sample, reanalysis is required for all samples analyzed after this highly concentrated sample which detected similar analytes.

5.6 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interference will vary considerably from one source to another depending upon the nature and complexity of the site being sampled. A silica gel SPE cleanup procedure is used to overcome many of these interferences, but some samples may require additional and more rigorous cleanup procedures which are beyond the scope of this method.

5.7 Other organic contaminants commingled with petroleum product releases, including chlorinated hydrocarbons, phenols, and phthalate esters, will be quantitated as Total and Extractable Petroleum Hydrocarbons. If necessary and/or desirable, additional sample cleanup and/or analytical procedures may be employed to minimize or document the presence of such compounds.

5.8 The leaching of plasticizers and other compounds have been observed from commercially available silica gel cartridges used to fractionate EPH sample extracts. Concerns of this nature must be continuously monitored and documented by analysis of Laboratory Method Blanks. Section 9.2 provides a procedure to eliminate or minimize this contamination.

5.9 Because of their weakly polar nature, naphthalene and substituted naphthalenes readily mobilize into the aliphatic extract if excessive amounts of hexane are used to elute the silica gel cartridge/column. Because these compounds constitute a significant percentage of the water-soluble fraction of fuel oils, this occurrence is especially problematic in the analysis of water samples. For this reason, the method requires the evaluation of the aliphatic fraction for the presence of naphthalene and 2-methylnaphthalene in the LCS/LCSD pair on a batch basis. The fractionation surrogate, 2-Bromonaphthalene, is used to monitor sample-specific fractionation efficiency.

6.0 SAFETY

6.1 The toxicity and carcinogenicity of chemicals used in this method have not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are available15-17 for the information of the analyst.

6.2 Methylene Chloride has been tentatively classified as known or suspected human or mammalian carcinogen:.

6.3 The toxicity of all solvents used in the laboratory have not been well defined. Susceptible individuals may experience adverse affects upon skin contact or inhalation of vapors. Therefore, protective clothing and gloves should be used and MeCl2 should be used only in a chemical fume hood or glove box. The same precaution applies to pure standard materials.

7.0 EQUIPMENT AND SUPPLIES

7.1 Sample Containers – 1 Lt screw cap amber glass bottles and PTFE-faced septa. If bottles are not certified pre-cleaned, prior to use and following each use, wash bottles and septa with detergent and tap water then rinse thoroughly with distilled water. Allow the bottles and septa to dry at room temperature, place only the bottles in an oven and heat to 200°C for 60 minutes. After removal from the oven allow the bottles to cool in an area known to be free of organics. After rinsing caps with distilled water, rinse in a beaker with HPLC grade or better acetone and place in a drying oven at 80°C for one hour.

7.1.1 Soil and sediment samples are collected in 4 oz. (120 mL) amber wide-mouth glass jars with Teflon-lined screw caps.

7.2 Auto-sanpler Vials – Agilent Auto-sampler vials, 2.0 ml vial with screw or crimp cap and a Teflon-faced septa.

7.3 Micro Syringes -- 10 µl, 25 µl 50 µl, 100 µl, 250 µl, and 1000 µl.

7.4 Pipettes – varied, Type A, TD, glass.

7.5 Volumetric Flask Type A-- 25 ml, 100 ml, 250 ml, and 500 ml.

7.6 Disposable Pasteur Pipettes, 9 inch -- Used for extract transfer.

7.7 Standard Solution Storage (SSS) Containers -- 10 ml Boston round, amber glass bottles with TFE-lined caps or equivalent.

7.8 Balance -- Analytical, capable of accurately weighing to the nearest 0.0001 g.

7.9 Glass funnels, 2-L Separatory funnels with Teflon stopcock (aqueous liquid-liquid extraction only)

7.10 Zymark Turbo-Vap, Kuderna-Danish Type Nitrogen blow-down concentrator apparatus including 1.0-mL graduated concentrator tube.

7.11 250-mL Erlenmeyer flasks

7.12 25-mL graduated cylinder

7.13 1-Liter graduated cylinder

7.14 100-mL beakers

7.15 Water bath: heated with a concentric ring cover or sand bath, capable of tempera ture control (± 2° C). The bath should be used in a hood.

7.16 Soxhlet, Soxtec or alternative extraction apparatus

7/17 Drying Oven and Desiccators

7.9 Gas Chromatography System

7.9.1 The GC is an Agilent model 6890 capable of temperature programming and equipped with Flame Ionization detector (FID), fused silica capillary column, splitless injector and a Agilent 100 position auto-sampler capable of injecting 1-4uL.

7.9.3 Primary Column - The analytical column must adequately resolve the n-C9 to n-C36 aliphatic hydrocarbon standard compounds and the Target PAH Analytes listed in Tables 1 and 2, respectively. Beckton uses the method recommended analytical capillary column RTX-5 (30-m x 0.32-mm i.d., 0.25-μm film thickness [Restek Corp. or equivalent]).

7.9.4 The analyst is permitted to modify GC columns, GC conditions, internal standard or surrogate compounds. Each time such method modifications are made they must be informed to the QA/QC officer and the analyst must repeat and produce acceptable data for the MDL & IDC procedures outlined in Section 10.4.

7.9.5 Chemstation data software capable of storing and reintegrating chromatographic data and capable of determining peak areas using a forced baseline projection.

7.0 REAGENTS AND STANDARDS

7.1 Reagents

7.1.1 Methylene Chloride High Purity Grade –It may be necessary to double distill the solvent if impurities are observed in the analytical target ranges.

7.1.2 n-Hexane High purity grade -- It may be necessary to double distill the solvent if impurities are observed in the analytical target ranges.

7.1.3 Acetone, High Purity -- Demonstrated to be free of analytes.

7.1.4 Methanol, High Purity -- Demonstrated to be free of analytes.

7.1.5 Silica Gel, 5-10gms, either prepared and packed by the laboratory, or purchased in 5 g/20-mL cartridges from a commercial vendor. Silica gel prepared and packed by the laboratory should be activated at 130°C for at least 16 hours, and heated to 150-160°C for several hours before use. Refer to Section 9.2.2 (in the referenced method) for guidance on the use of silica gel.

7.1.6 Sodium Sulfate, place in muffle furnace, increase temperature to 400°C and hold for a minimum of 30 minutes. Store this solution in a capped glass bottle not in a plastic container.

7.1.7 Stock Standard Reagents, purchase stock standard solutions at approximately 1000 ng/μL, purchase as certified solutions. Stock standard solutions must be replaced after 6 months, or sooner if comparison with check standards indicates a problem.

7.1.7.1 Aromatic Hydrocarbon Standard: The Aromatic Hydrocarbon Standard consists of the 17 PAH compounds listed in Table 2, a surrogate compound (i.e., ortho-terphenyl) and fractionation surrogate compounds.

7.1.7.2 Aliphatic Hydrocarbon Standard: The Aliphatic Hydrocarbon Standard consists of the 14 normal alkanes listed in Table 1, naphthalene, 2-methylnaphthalene, and a surrogate compound (i.e., 1- chloro-octadecane). Purchase stock standard solutions in Hexane.

7.1.7.3 Ammonium Chloride, NH4Cl, ACS Reagent Grade -- Used to convert free chlorine to monochloramine. Although this is not the traditional dechlorination mechanism, ammonium chloride is categorized as a dechlorinating agent in this method.

7.1.7.4 Calibration standards are prepared by serial dilution of the stock standard as described in Section 9.7.

7.1.7.5 The Petroleum Reference Spiking Solution consists of an API or commercial diesel fuel standard. Prepare stock standard solutions by ac-

curately weighing approximately 0.02500 g of neat product. Dissolve neat product in acetone and dilute to volume in a 10-mL volumetric flask. An appropriately diluted aliquot of the stock solution may be used to evaluate method performance.

7.2 Reagent Water -- Reagent water is defined as purified water which does not contain any measurable quantities of any target analytes or any other interfering species.

7.2.1 A Millipore Super-Q water system or its equivalent can be used to generate deionized reagent water. Distilled water that has passed through a charcoal filtered column (or two columns) has been found suitable.

7.2.2 The reagent water should be tested each day before it is used by analyzing a method blank as specified in **Section 11.0**.

7.3 Surrogate Stock Standard – The recommended surrogate standards are chloro-octadecane (COD, available from Restek Corporation, Bellefonte, PA) and ortho-terphenyl (OTP, available from EM Sciences, Gibbstown, NJ). Alternatively, 5-alpha-androstane may also be used as an aliphatic fraction surrogate without qualification.

7.3.1 The surrogate standard COD is prepared by accurately weighing approximately 0.0100 g of pure material in a 10-mL volumetric flask. Dissolve the material in hexane.

7.3.2 The surrogate standard OTP is prepared by accurately weighing approximately 0.0100 g of pure material in a 10-mL volumetric flask. Dissolve the material in methylene chloride.

7.3.3 Surrogate Spiking Solution: The recommended surrogate spiking solution is comprised of a mixture of the COD and OTP surrogate standards. Prepare a surrogate spiking solution which contains the surrogate standards at a concentration of 40 ng/μL in acetone or methanol. Each sample, blank, and matrix spike is fortified with 1.0 mL of the surrogate spiking solution. The use of higher concentrations are permissible and advisable when spiking highly contaminated samples.

7.4 Fractionation Surrogate Standards

7.4.1 The fractionation surrogate standards are added to the sample (hexane) extract just prior to fractionation. The purpose of the fractionation surrogate standards is to monitor the efficiency of the fractionation process, and ensure that unacceptable quantities of naphtha-

lene and substituted naphthalenes are not being eluted into the aliphatic extract.

7.4.2 The recommended fractionation surrogate standard is 2-Bromonaphthalene. Other alternative fractionation surrogate compounds, including 2-Fluorobiphenyl are permissible, provided that a demonstration is made that such compounds exhibit polarities (fractionation) properties similar to naphthalene.

7.4.3 The fractionation surrogate standards are prepared by accurately weighing approximately 0.0100 g of pure material in a 10-mL volumetric flask. Dissolve the material in Methylene Chloride.

7.5 Fractionation Surrogate Spiking Solution: is comprised of 2-Bromonaphthalene and 2-Fluorobiphenyl (optional) prepared in hexane at concentrations of 40 ng/μL. An aliquot of 1 mL of the fractionation surrogate spiking solution is added to the 1 mL EPH sample prepared extract. Alternative concentrations/volumes of the fractionation surrogate spiking solution are permissible.

7.6 **Internal Standard (IS)**

7.6.1 Internal standards are compounds with similar physical and chemical properties, and chromatographic compatibility with an analytical method's target analytes. ISs are added to all samples, both for analysis and quality control, at a known concentration and carried through the entire analytical process (extraction and analysis). Internal standards are used as the basis for quantification of target analyte compounds (and ranges) for the applied analytical method. **For the EPH Method, IS's are only utilized when GC/MS is utilized for quantification, because Beckton will use an FID, therefore no IS will be added.**

7.7 **Matrix Spiking Solution**

7.7.1 Analytes from each hydrocarbon group (i.e., aromatic and aliphatic hydrocarbons) are used in a matrix spiking solution, which is prepared using a separate source from the calibration standards.
7.7.2 The spiking solution, consisting of all normal alkanes in Table 1 and all PAHs in Table 2, is prepared in methanol or acetone at concentrations between 50 - 150 ng/μL (The concentration should be between the mid and upper level of calibration).

7.7.3 The samples selected as the matrix spike are fortified with 1.0 mL of the matrix spiking solution.

Analytical Note: The Matrix Spiking Solution should always be brought to room temperature before use to avoid the highest boiling (marginal solubility) hydrocarbon standards from coming out of solution.

7.8 **Fractionation Check Solution**

7.8.1 The Fractionation Check Solution is used to monitor the fractionation efficiency of the silica gel cartridge/column, and establish the optimum hexane volume required to efficiently elute aliphatic hydrocarbons while not allowing significant aromatic hydrocarbon breakthrough.

7.8.2 Prepare a Fractionation Check Solution in hexane containing 200 ng/μL of the Aliphatic Hydrocarbon standard (C9-C36 alkanes) and 200 ng/μL of the Aromatic Hydrocarbon standard (Target PAH Analytes). The final solution will contain 14 alkanes and 17 PAHs at concentrations of 200 ng/μL each. Alternative concentrations are permissible.

8.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

8.1 **Aqueous Samples**

8.1.1 It is good practice to instruct field personnel to collect aqueous samples in duplicate. Samples must be collected in 1 liter amber glass bottles with Teflon-lined screw caps.
8.1.2 Aqueous samples must be preserved at the time of sampling by the addition of a Hydrochloric acid to reduce the pH of the sample to less than 2.0. The addition of 5 mL of 1:1 HCl to a 1 liter sample should accomplish this. The uses of alternative acids are permissible. After collection and addition of acid, the sample must be cooled to 4± 2° C.

8.1.3 Aqueous samples must be extracted within 14 days of collection, and analyzed within 40 days of extraction.

8.2 **Soil/Sediment Samples**

8.2.1 Soil and sediment samples are collected in 4 oz. (120 mL) amber wide-mouth glass jars with Teflon-lined screw caps.

8.2.2 Soil and sediment samples must be cooled to 4 ± 2° C immediately after collection.

8.2.3 Soil and sediment samples must be extracted within 14 days of collection, and analyzed within 40 days of extraction.

9.0 SAMPLE ANALYSIS OF EXTRACTABLE PETROLEUM HYDROCARBONS (EPH)

9.1.1 Water Extraction by Separatory Funnel Liquid-Liquid Extraction.

9.1.1.1 Mark the meniscus on the 1 liter sample bottle (for later volume determination) and transfer the contents to a 2-liter separatory funnel. For blanks and quality control samples, pour 1 liter of reagent water into the separatory funnel. For all samples, blanks, LCSs, LCSDs and matrix spikes add 1.0 mL of the concentrated surrogate spiking solution (see Section 7.4) directly to the separatory funnel. For samples selected for spiking, also add 1.0 mL of the matrix spiking solution.

9.1.1.2 Check the pH of the sample with wide-range pH paper. Note the pH in the laboratory notebook. The pH of the sample must be adjusted to pH <2.

9.1.1.3 Add 60 mL methylene chloride to the sample bottle to rinse the inner walls of the container, then add this solvent to the separatory funnel.

9.1.1.4 Seal and shake the separatory funnel vigorously for at least three (3) minutes with periodic venting to release excess pressure.

NOTE: Methylene chloride creates excessive pressure very rapidly; therefore, venting should be done immediately after the separatory funnel has been sealed and shaken once.

9.1.1.5 Allow the organic layer to separate from the water phase for a minimum of 5 minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the solvent extract in an Erlenmeyer flask.

9.1.1.6 Repeat the extraction two more times using additional 60 mL portions of solvent. Combine the three solvent extracts in a 250-mL Erlenmeyer flask. (Steps 9.1.1.3 to 9.1.1.5)

9.1.1.7 For sample volume determination add water to the sample bottle to the level of the meniscus previously marked and transfer this water to a graduated cylinder.

9.1.1.8 Dry the extract by passing it through a glass powder funnel containing anhydrous sodium sulfate or other suitable drying agent. Collect the dried extract in a Zymark concentrator tube. Rinse the Erlenmeyer flask, which contained the solvent extract, with 20 to 30 mL of methylene chloride and add it to the funnel to complete the quantitative transfer.

9.1.1.9 Place the tube in a Zymark concentrator evaporation well.

9.1.1.10 When the apparent volume of liquid reaches 1 mL, remove the tube from the water bath and allow it to drain and cool for at least 10 minutes.

9.1.1.11 Exchange the methylene chloride with hexane by adding 50 mL of hexane to the tube. Concentrate the extract to less than 1 ml.

9.1.1.12 Remove the flask from the well when the unit signals the 1-mL concentrator volume. If the extract is highly colored, forms a precipitate, or stops evaporating, the final volume should be higher. If a TPH analysis is to be conducted, without fractionation, proceed to Section 9.3.3

Analytical Note: Due caution must be exercised during blowdown to avoid losses of the more volatile (C9 through C12) EPH components. The fractionation extract (or any extract) volume should never be reduced below 1 mL in this or any other step to minimize volatilization losses.

9.1.1.13 Add 1 mL of the concentrated fractionation surrogate (see Section 7.5) spiking solution to the 1 mL hexane extract. The concentrated matrix spiking solution (see Section 7.7) should also be added at this time, as required.

9.1.1.14 Record the sample preparation information for the extraction and concentration steps. At a minimum, record the date, sample laboratory number, sample volume, volume and concentration of added surrogates and matrix spike solutions, final extract volume, and any deviations or problems associated with the extraction of the samples.

9.1.1.15 The 2 mL extract (1 mL extract + 1 mL fractionation surrogate) is now ready to be cleaned and fractionated using either commercially-available or self-packed silica gel SPE cartridges. If cleanup will not be performed immediately, transfer the extract to a Teflon lined screw-cap vial, label, and refrigerate.

9.1.1.16 For cleanup and fractionation, refer to Section 9.2.

9.1.2. Soil and/or Sediment Extraction

9.1.2.1 Blend 10 g of the solid sample with 10 g anhydrous sodium sulfate and place in an extraction flask. Add 1.0 mL of the surrogate spiking solution (see Section 7.4) to all samples, blanks, LCSs, LCSDs and matrix spikes. Thoroughly mix the surrogate spiking solution into the sample. For samples selected for spiking, add 1.0 mL of the matrix spiking solution. Thoroughly mix the matrix spiking solution(s) into the sample.

9.1.2.2 Place 300 mL of methylene chloride into a 500-mL flask. Attach the flask to the extractor and extract the sample for 16-24 hr. Volume of methylene chloride should be adjusted to accommodate the size of the flask utilized.

9.1.2.3 Allow the extract to settle after the extraction is completed.

9.1.2.4 Turn on the Zymark concentrator and let the unit reach temperature.

9.1.2.5 Dry the extract by passing it through a glass powder funnel containing anhydrous sodium sulfate or other suitable drying agent. Collect the dried extract in a Zymark concentrator tube. Rinse the Erlenmeyer flask, which contained the solvent extract, with 100 to 125 mL of methylene chloride and add it to the funnel to complete the quantitative transfer.

9.1.2.6 Place on the evaporator, when the apparent volume of liquid reaches 1 mL, remove the tube from the water bath and allow it to drain and cool for at least 10 minutes.

9.1.2.7 Exchange the methylene chloride with hexane by adding 50 mL of hexane to the tube. Concentrate the extract to less than 1 ml.

Analytical Note: Due caution must be exercised during blowdown to avoid losses of the more volatile (C9 through C12) EPH components. The fractionation extract (or any extract) volume should never be reduced below 1 mL in this or any other step to minimize volatilization losses.

9.1.2.8 Add 1 mL concentrated fractionation surrogate (see Section 7.5) spiking solution to the 1 mL hexane extract.

9.1.2.9 Record the sample preparation information for the extraction and concentration steps. At a minimum, record the date, sample laboratory number, sample weight, volume and concentration of added surrogates and matrix spike solutions, extraction start and stop times, final extract volume and any deviations or problems associated with the extraction of the samples.

9.1.2.10 The 2 mL extract (1 mL extract + 1 mL fractionation surrogate) is now ready to be cleaned and fractionated using silica gel SPE. If cleanup will not be performed immediately, transfer the extract to a Teflon-lined screw-cap vial, label, and refrigerate.

9.1.2.11 For cleanup and fractionation, refer to Section 9.2.

9.2 **Silica Gel Cleanups and Fractionation**

NOTE: The Silica Gel Cleanup and Fractionation step is a critical and highly sensitive procedure. Small changes in the volumes of eluting solvents, fractionation equipment, and/or fractionation techniques can significantly impact the proportion of hydrocarbons segregated in either the aliphatic or aromatic fractions. Considerable care and attention is required to ensure satisfactory results.

9.2.1 Each sample fractionation requires 1 mL of sample extract. Because 2 mL of sample extract are available, two fractionations may be undertaken for each sample. Refractionation would be necessary if problems are experienced during the initial fractionation effort, if unacceptable breakthrough is noted for naphthalene and 2-methylnaphthalene in the LCS

and/or LCSD, and/or if unacceptable recoveries are noted for the fractionation surrogate standard. The extra volume of sample extract is also provided to facilitate initial (unfractionated) TPH screening of a sample, to obtain a GC/FID "fingerprint", and/or to determine whether sufficient total hydrocarbons are present to warrant fractionation and comparison to risk-based cleanup standards.

9.2.2 Silica gel is a regenerative adsorbent of amorphous silica with weakly acidic properties. It is produced from sodium silicate and sulfuric acid. Silica gel can be used for column chromatography and is used for separating analytes from interfering compounds of a different chemical polarity. Silica gel is also used to separate petroleum distillates into aliphatic and aromatic fractions. A 5 g/20 mL Solid Phase Extraction (SPE) silica gel cartridge is commercially available. Alternatively, the use of self-packed columns of activated silica gel may also be used. The use of activated silica gel for general column chromatographic applications is described in detail SW-846 Method 3630C.

To ensure satisfactory fractionation, silica gel/cartridges must not be overloaded. It is recommended that loading be limited to no more than 5 mg total hydrocarbons/gram silica gel; for a 1 mL extract fractionated on a 5 gram silica gel cartridge, this would equate to a hydrocarbon extract loading of no greater than 25,000 mg/L. It should be noted that overloading the column may result in a premature breakthrough of the C**11**-C**22** aromatic hydrocarbon range. If overloading is encountered, the sample must be re-fractionated at a dilution appropriate for the column's maximum loading capacity.

Unsealed silica gel/cartridges must be stored in a properly-maintained desiccators to avoid inadvertent adsorption of ambient moisture. Silica gel that has been exposed to moisture may perform erratically resulting in poor performance manifested by naphthalene/2-methylnaphthalene and fractionation surrogate breakthrough.

Analytical Note: Air-drying of the cartridges may adversely affect silica gel performance do not air-dry a cartridge.

9.2.3 If concerns exist over the presence of contaminants in the silica gel/cartridge, pre-rinse the column with 30 mL of methylene chloride.

9.2.3.1 Rinse the column with 30 mL of hexane, or 60 mL if pre-rinsed with methylene chloride per Section 9.2.3. Let the hexane flow through

the column until the head of the liquid in the column is just above the column frit. Close the stopcock to stop solvent flow. Discard the collected hexane used for cleaning.

9.2.3.2 Load 1.0 mL of the combined sample extract and fractionation surrogate solution onto the column. Open the stopcock, and start collecting elutant immediately in a 25-mL volumetric flask labeled "aliphatic".

9.2.3.3 Just prior to exposure of the column frit to the air, elute the column with an exactly additional 19 mL of hexane, so that a total of approximately 20 mL of hexane is passed through the column.

It is essential that "constant flow" of the sample extract be achieved through the silica gel cartridge/column. Hexane should be added in 1-2 mL increments or dropwise using a pipet, with additions occurring when the level of solvent drops to the point just prior to exposing the column frit to air. The use of a stopcock is mandatory. Care must be taken to ensure that the silica gel is uniformly packed in the column. The analyst must be observant of any channeling, streaking, or changes in the silica gel matrix during fractionation; if any of these occur, the procedure must be repeated with another 1 mL volume of sample extract.

The amount of hexane used during fractionation is critical. Excessive hexane - as little as 0.5 mL - can cause significant elution of lighter aromatics into the aliphatic fraction. Insufficient hexane will cause low recoveries of the aliphatic fraction. The volume of the hexane fractionation elutriate should not exceed 20 mL.

9.2.3.4 The Fractionation Check Solution described in Section 7.8 must be used to evaluate each new lot of silica gel /cartridges to re-establish the optimum volume of hexane elutriate. See Appendix 5, Section 5.0 of the referenced method for optimization specifications. It is not uncommon to encounter inconsistent cartridge weights, mesh sizes and/or variable fractionation performance within the same lot of silica gel cartridges. Therefore, perform fractionation performance checks particularly per lots of silica gel cartridges. Additional performance checks are required at a rate of 1 per 50 cartridges.

9.2.3.5 Following recovery of the aliphatic fraction, elute the column with 20 mL of methylene chloride and collect the eluant in a 25 mL volumetric flask. Label this fraction "aromatics".

9. 3 **Final Sample Extract Concentration**

9.3.1 Transfer the contents of the 25.0 mL "aliphatics" (in hexane) and "aromatics" (in methylene chloride) volumetric flasks into separate labeled graduated Zymark concentrator tubes. Concentrate each of the extracts to a final volume of 1 mL under a gentle stream of air or nitrogen.

Analytical Note: Due caution must be exercised during blow-down to avoid losses of the more volatile (C9 through C12) EPH components. The fractionation extract (or any extract) volume should never be reduced below 1 mL in this or any other step to minimize volatilization losses.

9.3.2 Transfer the final 1 mL extracts from each concentrator tube to labeled two-mL glass auto-sampler vials with Teflon-lined rubber crimp caps. If appropriate, add an internal standard at the appropriate concentration.

9.3.3 Proceed with the analysis in accordance with Analyze all laboratory method blanks and QC samples under the same conditions as that used for samples.

9.4 **Determination of Percent Moisture**

9.4.1 Soil and sediment results must be reported on a dry-weight basis.

9.4.2 Transfer 5 to 10 g of sample into a tared (± 0.1 g) crucible and determine "wet weight". This sample must be obtained from a vial or container that does not contain methanol. Dry this 5 to 10 g sample overnight at 105° C. Allow crucible to cool in a desiccators and reweigh (± 0.1 g). Re-desiccate for 1 hour and verify "dry weight". Calculate the percent moisture.

9.5 **Analytical Conditions**

9.5.1 Recommended analytical conditions are presented below. The chromatographic column: Restek RTX-5, 30 m x 0.32 mm I.D., 0.25 μm film or an equivalent with chromatographic properties.

<u>Conditions</u>
Oven Temperature Program: Initial oven temperature 60° C, hold time 1 min; to 290 ° C @ 8° C/min, hold time 6.75 min
Total Run Time: 36.5 min

Sample/auto-sampler Injection 1-4 uL
Gas Flow Rates: Carrier gas - Helium @ 2 to 3 mL/ min
Oxidizer - Air @ 400 mL/min
Fuel - Hydrogen @ 35 mL/min
Make up - Air @ 30.0 mL/min
Injection Port Temperature: 285° C
Column Inlet Pressure: 15 p.s.i.g.
Detector Temperature: 315° C (FID)
Linear Velocity: 50 cm/sec

9.5.2 GC Maintenance

9.5.2.1 Insert liners for Capillary columns: replace with deactivated injection liners, the glass injection port insert or replace with a cleaned and deactivated insert.

9.5.2.2 Capillary Column: Break off the first few inches, up to one foot, of the injection port side of the column.

9.5.2.3 Remove the column and solvent back-flush according to the manufacturer's instructions.

9.5.2.4 Bake out the column at the maximum temperature of the temperature program. If these procedures fail to eliminate a column degradation problem, it may be necessary to replace the column.

9.6 **Retention Time Windows**

9.6.1 Before establishing retention time windows, optimize the GC system's operating conditions. Make three injections of the Aromatic Hydrocarbon and Aliphatic Hydrocarbon standard mixtures throughout the course of a 72-hr period. Serial injections over less than a 72-hr period may result in retention time windows that are too restrictive.

9.6.2 Calculate the standard deviation of the three absolute retention times for each individual component in the Aromatic Hydrocarbon standard, the Aliphatic Hydrocarbon standard, and all surrogates and internal standards.

9.6.3 The retention time window is defined as plus or minus three times the standard deviation of the absolute retention times for each compound

in the Aliphatic and Aromatic Standards. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

9.6.4 In those cases where the standard deviation for a particular standard is close to zero the default value of 0.1 minutes should be used. Alternatively, the laboratory may substitute the standard deviation of a closely eluting structurally similar compound to develop a representative statistically-derived retention time window.

9.6.5 The laboratory must calculate retention time windows for each compound in the Aliphatic and Aromatic Standards on each GC column and whenever a new GC column is installed. These data must be retained by the laboratory.

9.6.6 EPH retention time (RT) windows are defined as beginning 0.1 minutes before the RT of the beginning marker compound and ending 0.1 minutes after the RT of the ending marker compound, except for n-C19, which is both a beginning and ending marker compound for two different ranges.

The C9 - C18 Aliphatic Hydrocarbon range ends immediately (0.1 min) before the elution of the n-C19 peak. The C19 - C36 Aliphatic Hydrocarbon range begins 0.1 min before the elution of the n-C19 peak; therefore there is no overlap of the two ranges and the n-C19 peak is only included in the C19 - C36 Aliphatic Hydrocarbon range.

EPH marker compounds and windows are summarized in Table 3.

Table 3
EPH Marker Compounds and Windows

Hydrocarbon Range	Beginning Marker	Ending Marker
C9-C18 Aliphatic Hydrocarbons	0.1 min before n-Nonane	0.1 min before n-Nonadecane
C19-C36 Aliphatic Hydrocarbons	0.1 min before n-Nonadecane	0.1 min after n-Hexatriacontane
C11-C22 Aromatic Hydrocarbons	0.1 min before Naphthalene	0.1 min after Benzo (g,h,i) Perylene

9.6.7 If a TPH analysis is done without fractionation, TPH retention time (RT) windows are defined as beginning 0.1 minutes before the RT of n-Nonane and ending 0.1 minutes after the RT of n- Hexatriacontane.

9.7 **Calibration**

9.7.1 Internal Standard Calibration Procedure: An internal standard calibration procedure **is not recommended** for this method except when GC/MS is used to quantify target PAH Analytes and hydrocarbon ranges.

9.7.2 External Standard Calibration Procedure: The use of Calibration Factors (CF) is the preferred approach to determine the relationship between the detector response and the analyte and collective range concentrations. It is also permissible to utilize linear regression to calculate the slope and y-intercept that best describes the linear relationship between the analyte and collective range concentrations and the instrument response.

9.7.2.1 Prepare Aromatic and Aliphatic Hydrocarbon calibration standards from the Stock Standard Solution (in methanol) at a minimum of five concentrations (i.e., 1x, 10x, 50x, 100x and 200x) by adding volumes of one or more stock standard solutions to volumetric flasks and diluting to volume with methylene chloride and hexane, respectively. The surrogate OTP and the fractionation surrogates are included in the Aromatic Hydrocarbon Standard; the surrogate COD is included in the Aliphatic Hydrocarbon Standard. The lowest concentration (1x) determines the minimum working range of the calibration curve and defines the Reporting Limit (RL) for individual Target Analytes. The highest concentration (200x) defines the maximum upper working range of the calibration curve. Target analytes may not be reported above this concentration without sample dilution. RLs for collective EPH aliphatic and aromatic hydrocarbon ranges are discussed in Section 12.0.The collective concentrations of individual EPH aliphatic and aromatic hydrocarbon ranges are provided in Table 4.

Table 4. Recommended Calibration Standard Concentrations (1 µL Injection)

	Concentration (ug/L)

Component	1X	10X	50X	100X	200
Total Concentration C9 - C18 Aliphatic Hydrocarbons (6 components)	6	60	300	600	1200
Total Concentration C19 - C36 Aliphatic Hydrocarbons (8 components)	8	80	400	800	1600
Total Concentration C11 - C22 Aromatic Hydrocarbons/ PAHs (17 components)	17	170	850	1700	3400

9.7.2.2 Introduce each calibration standard into the gas chromatograph using the injection volume (e.g., 1 to 4 μL) that will be used to introduce the "actual" samples and following the procedures outlined in Section 9.8.

9.7.2.3 Target PAH Analyte Calibration: Tabulate peak area responses against the concentration injected. The ratio of area response to the concentration injected, defined as the calibration factor (CF), can be determined by the data software The percent relative standard deviation (%RSD) of the calibration factor must be equal to or less than 25% over the working range for the analyte of interest. When this condition is met, linearity through the origin may be assumed, and the average calibration factor may be used in lieu of a calibration curve .

9.7.2.4 Hydrocarbon Range Calibration (External Standard): A calibration factor must also be established for each hydrocarbon range of interest. Calculate the CFs for C9-C18 Aliphatic Hydrocarbons, C19-C36 Aliphatic Hydrocarbons and C11-C22 Aromatic Hydrocarbons from the appropriate FID chromatogram. Tabulate the summation of the peak areas of all components in that fraction (i.e. C9-C18 Aliphatic Hydrocarbons, 6 components) against the total concentration injected. The results can be used to calculate the ratio of the peak area response summation to the concentration injected, defined as the CF, for the hydrocarbon ranges using the chemstation software. The %RSD of the calibration factor must be equal to or less than 25% over the working range for the hydrocarbon range of interest, as determined using Equation 2.

A listing of the collective nominal concentrations of standards within each hydrocarbon range is provided in Table 4.

Note: For the calculation of calibration factors (CFs): The area for the surrogates must be subtracted from the area summation of the range in which they elute (e.g., COD is subtracted from the C19 - C36 Aliphatic Hydrocarbon range). It must also be subtracted when calculating ranges in samples, blanks, standards and QC's
The areas associated with naphthalene and 2- methylnaphthalene in the aliphatic range standard must be subtracted from the uncorrected collective C9-C18 Aliphatic Hydrocarbon range area prior to calculating the CF.

9.7.2.5 At a minimum, the calibration factor must be verified on each working day, after every 20 samples or every 24 hours (whichever is more frequent), and at the end of the analytical sequence by the injection of a mid-level continuing calibration standard to verify instrument performance. If the percent difference (%D) for any analyte varies from the predicted response by more than ±25%, as determined using the chemstation software, a new five-point calibration must be performed for that analyte. Greater percent differences are permissible for n-nonane. If the %D or percent drift for n-nonane is greater than 30%, note the nonconformance in the case narrative It should be noted that the %Ds are calculated when CFs are used for the initial calibration and percent drifts are calculated when calibration curves using linear regression are used for the initial calibration.

9.7.2.6 For TPH analysis, without fractionation, calibration factors are developed based upon the response of all 14 aliphatic components using the chemstation software.

9.8 **GC Analysis**

9.8.1 Samples are analyzed in a group referred to as an analytical batch. For methods that require extraction prior to analysis, such as EPH, the number of samples that comprise an analytical batch is generally limited to 20 samples plus the requisite QC samples processed concurrently with the extraction batch. The analytical sequence begins with instrument calibration (initial or continuing) followed by up to 20 samples interspersed
with blanks and other QC samples and closed with a mid-range continuing calibration standard. The analytical sequence ends when one or more analytical batches have been processed or when any required qualitative and/or quantitative QC criteria are exceeded.

9.8.2 Aliphatic and aromatic extracts are introduced into the gas chromatograph by direct injection.

9.8.3 Inject 1 to 4 μL of the sample extract using the solvent flush technique. Smaller volumes may be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 μL and the resulting peak size in area units. It is required that the sample and calibration standard injection volume be consistent.

9.8.4 Establish daily retention time windows for each analyte of interest. Use the absolute retention time for each analyte as the midpoint of the window for that day. The daily retention time window equals the midpoint ± three times the standard deviation determined in Section 9.6. Alternatively, the default value of 0.1 minutes may be used for the daily retention time window.

9.8.4.1 When identifying individual PAH's. tentative identification of a Target PAH Analytes occurs when a peak from a sample chromatogram falls within the daily retention time window. Confirmation on a second GC column or by GC/MS analysis may be necessary, if warranted by project's data quality objectives (DQO). If not required under the DQO the result obtained is reported as present, the analytical narrative should state that the hit was not confirmed.

9.8.4.2 Validation of GC system qualitative performance must be accomplished by the analysis of mid-level standards within the analysis sequence. If the retention times of the Target PAH Analytes fall outside their daily retention time window in the standards, the system is out of control. In such cases, the cause of the non-conformance must be identified and corrected.

9.8.5 Aliphatic and aromatic ranges of interest are determined by the collective integration of all peaks that elute between specified range "marker" compounds.

Analytical Note: During the method validation (or if software versions change), collective peak area integration (peak summation by the software) must be manually verified to document accurate integration.

9.8.6 **When quantifying on a peak area basis by external calibration, collective peak area integration for the fractional ranges, or TPH, must be from baseline (i.e. must include the unresolved complex mixture "hump" areas).**

For the integration of individual Target PAH Analytes, surrogate compounds, and internal standards, a valley-to-valley approach is be used, though this approach may be modified on a case-by-case basis by an experienced analyst. In any case, the unresolved complex mixture "hump" areas must not be included in the integration of individual Target PAH Analytes, surrogate compounds, and internal standards.

9.8.7 Software baseline correction using a system solvent blank is **only** permissible for the calculation of aliphatic and aromatic hydrocarbon range concentrations when conducted in accordance with the procedures and requirements specified in Section 11.2.5 of the referenced method.

9.8.8 If the Target or Diesel PAH Analytes are to be quantitated using this method, and the response for an individual analyte exceeds the highest calibration concentration, dilute the extract and reanalyze. The samples must be diluted so that all peaks fall within the calibration range of the detector and are bracketed by upper and lower calibration standards.

9.8.9 For non-target analytes eluting in the aliphatic, aromatic or TPH fractions, the upper linear range of the system should be defined by peak height measurement, based upon the maximum peak height documented for an aliphatic or aromatic standard within the fraction that is shown to be within the linear range of the detector. In other words, dilute out of range samples based on peak height and calculate for reporting the diluted fraction within range.

9.8.10 Analytical conditions that require sample dilution include;

1. The concentration of one or more of the target analytes exceed the concentration of their respective highest calibration standard,
2. Any non-target peak eluting within any aliphatic or aromatic range exceeds twice the peak height documented for the highest range-specific calibration standard, or

3. Anytime a saturated chromatographic peak (flat-topped peak) is encountered
   When sample extracts are diluted, the Reporting Limit (RL) for each target analyte and/or range must be adjusted (increased) in direct proportion to the Dilution Factor (DF).

Where:

$$\text{Adjusted DF} = \frac{\text{Sample Extract Volume (mL) + Diluent Volume (mL)}}{\text{Sample Extract Volume (mL)}}$$

Analytical Note: It should be understood that samples with elevated RLs as a result of a dilution may not be able to satisfy "MCP program" reporting limits in some cases if the adjusted RL is greater than the applicable MCP standard or criterion to which the concentration is being compared. Such increases in RLs are the unavoidable but acceptable consequence of sample extract dilution that enable quantification of target analytes which exceed the calibration range. All dilutions must be fully documented in the analytical report.

Analytical Note: Over dilution is an unacceptable laboratory practice. The target post-dilution concentration for the highest concentration target analyte should be at least 60 - 80% (must be at least 50%) of its highest calibration standard. This will avoid unnecessarily high reporting limits for other target analytes, which did not require dilution.

9.9 **Calculations**

9.9.1 External Standard Calibration: The concentration of Target PAH Analytes and hydrocarbon ranges in a sample may be determined by calculating the concentration of the analyte or hydrocarbon range injected, from the peak area response, using the calibration factor determined in Section 9.7.2. If linear regression is used for calibration, refer to Appendix 4 of the referenced method for sample concentration calculations.

9.9.2 Aqueous Samples (External standard): The concentration of a specific analyte or hydrocarbon range in an aqueous sample may be calculated using Equations 1 and 2, respectively.

Equation 1: Aqueous Samples (Target PAH Analytes: External Standard):

Concentration Analyte (μ g/L)= (Ax)(D) (Vt)/ (CF) (Vs)

Equation 2: Aqueous Samples (Hydrocarbon Ranges and TPH: External Standard):

Concentration HC Range or TPH (μ g/L)= (As)(D)(V*t*) / (Range CF) (Vs)

where:

A_s = Response for the analyte, hydrocarbon range, or TPH in the sample. Units must be in area counts for Target PAH Analytes and must be an area count summation for the hydrocarbon ranges and TPH.

D = Dilution factor; dimension-less.

CF = Average Calibration Factor for Target PAH Analyte, determined in Chemstation.

Range CF = Average Calibration Factor for hydrocarbon range or TPH, determined in Chemstation.

V_t = Volume of total extract, μL (fractionation + surrogate volume)

V_s = Volume of sample extracted, mL.

9.9.3 Non-aqueous samples (External Standard): The concentration of a specific analyte or hydrocarbon range in a non-aqueous sample may be calculated using Equations 3 and 4, respectively.

Equation 3: Non-Aqueous Samples (Target PAH Analytes: External Standard)

Concentration Analyte (ug/kg)= (A_s)(V_t)(D) / (W_d)(CF)

Equation 4: Non-Aqueous Samples (Hydrocarbon Ranges and TPH: External Standard)

Concentration HC Range or TPH (ug/kg)= (A_s)(V_t)(D) / (W_d)(Range CF)

where:

W_d = Dry weight of sample, g;

W_d (g) = (% Dry Solids / 100)(g of extracted sample)

A_s = Response for the analyte, hydrocarbon range, or TPH in the sample. Units must be in area counts for Target PAH Analytes and must be an area count summation for the hydrocarbon ranges and TPH.

D = Dilution factor; dimension-less.

CF = Average Calibration Factor for Target PAH Analyte, determined in Chemstation

Range CF = Average Calibration Factor for hydrocarbon range or TPH, determined in Chemstation.

V_t = Volume of total extract, μL (fractionation + surrogate volume)

10.0 QUALITY CONTROL

General Requirements and Recommendations

10.1 Beckton Environmental Laboratories, Inc., operates a fo performance check standard, initial demonstration of laboratory capability, method detection limit determination, analysis of laboratory reagent blanks, continuing calibration check standard, laboratory fortified sample matrices, field duplicates and monitoring surrogate and/or monitoring internal standard peak response in each sample, standard and blank. Additional quality control practices may be added.

10.2 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of analyst capability (IDC) and an ongoing analysis of spiked samples to evaluate and document the quality of data. The initial demonstration of analyst capability should be repeated whenever new staff are trained or significant changes in instrumentation or the method (i.e., new extraction method, etc.) are made. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance standards for the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be ana-

lyzed to confirm that the analytical system was in-control when the measurements were performed.

10.3 A system solvent blank must be run after all highly contaminated samples to minimize the potential for sample carryover. For purposes of this analytical requirement, any sample with an on-column concentration greater than the highest calibration standard is considered “highly contaminated” (any subsequent sample with a positive hit must be a suspected cross-contaminated sample).

10.4 Batch Analytical Quality Control Samples

10.4.1 At a minimum, for each analytical batch (up to 20 samples) or every 24 hours, whichever come first, a beginning and ending Continuing Calibration Standard must be analyzed. For analytical batches with more than 10 samples, the analysis of an additional mid-range Continuing Calibration Standard should also be considered. However, it should be noted that the analysis of the Continuing Calibration Standard is required prior to sample analysis, after every 20 samples or every 24 hours, whichever come first, and at the end of an analytical sequence, at a minimum.

10.4.2 At a minimum, for each analytical batch (up to 20 samples of similar matrix), a Laboratory Method Blank, a Laboratory Control Sample (LCS), and a LCS Duplicate must also be analyzed and results analyzed as part of Beckton’s continuing quality control program. The blank and quality control samples fortified with known concentrations and volumes of analytical standards should be carried through the complete sample preparation and measurement processes.

10.4.3 It should be noted that field QC samples (field blanks, duplicates, matrix spikes and matrix spike duplicates) are run on pre-identified field samples at the request of the data user. Coordination with the client is required to assure that adequate sample volume is available.

10. 4.4 The recommended analytical sequence is as follows:

(1) Analytical Batch Opening Initial Calibration (performed initially)
(2) Initial Calibration Verification
(3) Extraction Batch Laboratory Control Sample (second source)

(4) Extraction Batch Laboratory Control Sample Duplicate (second source)
(5) Extraction Batch Laboratory Method Blank
(6) Up to 10 Samples
(7) Matrix Duplicate sample
(8) Matrix Spike/MS Duplicate
(9) mid-range Continuing Calibration Standard (after 10 samples)
(10) Closing mid-range or Continuing Calibration Standard a after 10 samples and at end of analytical batch. May be used as Analytical Batch Opening Continuing Calibration for the next analytical batch if batches are processed continuously.

10.4. 5 It is recommended that surrogate standard recoveries be monitored and documented on a continuing basis. At a minimum, when surrogate recovery from a sample, blank, or QC sample is less than 40% or more than 140%, check calculations to locate possible errors, check the fortifying solution for degradation, and check for changes in instrument performance. If the cause cannot be determined, re-extract and reanalyze the sample if the recovery of one surrogate is <40% or the recoveries of both surrogates are outside the acceptance limits. The laboratory may first reanalyze the archived portion (prior to fractionation) to see if the surrogate recoveries were possibly affected by fractionation. If surrogate recoveries are acceptable in the archived portion, re-fractionation and reanalysis of the archived extract must be performed. Re-extraction and reanalysis are not required if one of the following exceptions applies:

(1) Obvious interference is present on the chromatogram (e.g., unresolved complex mixture); and
(2) If the surrogate exhibits high recovery and associated target analytes or hydrocarbon ranges are not detected in sample.

Analysis of the sample on dilution may diminish matrix-related surrogate recovery problems. This approach can be used as long as the reporting limits to evaluate applicable MCP standards can still be achieved with the dilution. If not, reanalysis without dilution must be performed.

10.5 **Minimum Instrument QC**

10.5.1 The instrument must be able to achieve adequate separation and resolution of peaks and analytes of interest.

10.5..1 The n-nonane (n-C9) peak must be adequately resolved from the solvent front
of the chromatographic run.

10.5..2 The surrogates COD and OTP must be adequately resolved from any individual
components in the Aliphatic Hydrocarbon and Aromatic Hydrocarbon standards.

10.5..3 All peaks of interest in the Aliphatic Hydrocarbon standard must be adequately
resolved to baseline. In the Aromatic Hydrocarbon standard, baseline separation is expected for Phenanthrene and Anthracene. Benzo(a)Anthracene, Chrysene, benzo(b)Fluoranthene, Benzo(k)fluoranthene, Dibenzo(a,h)Anthracene, and Indeno(1,2,3-cd)Pyrene are not expected to be chromatographically separated to baseline and may be reported as an unresolved mixture, unless adequate resolution is obtained .

For the purposes of this method, adequate resolution is assumed to be achieved if the height of the valley between two peaks is less than 25% of the average height of the two peaks.

10.5.4 Retention time windows must be re-established for Target EPH Analytes each time a new GC column is installed, and must be verified and/or adjusted on a daily basis. (See Sections 9.6 and 9.8.4 of the referenced method).

10.5.5 Calibration curves, calibration factors, or response factors must be developed based upon the analysis of calibration standards prepared at a minimum of 5 concentration levels. The linearity of calibration or response factors may be assumed if the %RSD over the working range of the curve is less than or equal to 25%. Alternatively, if linear regression analysis is used for quantitation (i.e., calibration curve), the correlation coefficient (r) must be at least 0.99.

10.5.6 In order to demonstrate the absence of aliphatic mass discrimination, the response ratio of C28 to C20 must be at least 0.85. If <0.85, this nonconformance must be noted in the laboratory case narrative. The chromatograms of Continuing Calibration Standards for aromatics must be reviewed to ensure that there are no obvious signs of mass discrimination.

10.5.7 Due care must be exercised to assure that the peaks for naphthalene and n-dodecane in the aliphatic hydrocarbon fraction are adequately resolved to allow for an accurate determination of the naphthalene concentration in the LCS/LCSD pair.

10.6 **Initial and Periodic Method QC Demonstrations**

The QC procedures described in Appendix 5 (of the referenced method) and described in SW-846 Method 8000B, Section 8.4 must be conducted, successfully completed and documented as an initial demonstration of analyst capability (IDC), prior to the analysis of any samples by the EPH Method. Subsequent to this initial demonstration, additional evaluations of this nature should be conducted on a periodic basis, in response to changes in instrumentation or operations, training new analysts and/or in response to confirmed or suspected systems, method, or operational problems. Elements of the Initial Demonstration of Laboratory Capability include:

10.6.1 Demonstration of Acceptable System Background,
10.6.2 Initial Demonstration of Accuracy (IDA),
10.6.3 Initial Demonstration of Precision (IDP),
10.6. 4 Initial Demonstration of Fractionation Efficiency, see Appendix 5, Section 5.0 (of the referenced method), and
10.6.5 Method Detection Limit (MDL),

10.7 **Ongoing Method QC Demonstrations**

10.7.1 Each sample, blank, LCS, LCSD, MS, and Matrix Duplicate must be fortified with the surrogate spiking solution. Required surrogate recovery is 40% to 140%. At a minimum, when surrogate recovery from a sample, blank, or QC sample is less than 40% or more than 140%, check calculations to locate possible errors, check the fortifying solution for degradation, and check for changes in instrument performance. If the cause cannot be determined, re-extract and reanalyze the sample if the recovery of one surrogate is <40% or the recoveries of both surrogates are outside the acceptance limits. The laboratory may first reanalyze the archived portion (prior to fractionation) to see if the surrogate recoveries were possibly affected by fractionation. If surrogate recoveries are acceptable in the archived portion, re-fractionation and reanalysis

of the archived extract must be performed. Re-extraction and reanalysis are not required if one of the following exceptions applies:

(1) Obvious interference is present on the chromatogram (e.g., unresolved complex mixture); and
(2) If the surrogate exhibits high recovery and associated target analytes or hydrocarbon ranges are not detected in sample.

Analysis of the sample on dilution may diminish matrix-related surrogate recovery problems. This approach can be used as long as the reporting limits to evaluate applicable MCP standards can still be achieved with the dilution. If not, reanalysis without dilution must be performed.

10.7.2 Each sample (field and QC sample) must be evaluated for potential breakthrough on a sample-specific basis by evaluating the % recovery of the fractionation surrogate (2-bromonaphthalene) and on a batch basis by quantifying naphthalene and 2-methylnaphthalene in both the aliphatic and aromatic fractions of the LCS and LCSD. **If either the concentration of naphthalene or 2- methylnaphthalene in the aliphatic fraction exceeds 5% of the total concentration for naphthalene or 2-methylnaphthalene in the LCS or LCSD, fractionation must be repeated on all archived batch extracts.** If the fractionation surrogate recovery is outside the 40 - 140% limits, then fractionation must be repeated on the archived extract of the affected sample.

NOTE: The total concentration of naphthalene or 2-methylnaphthalene in the LCS/LCSD pair includes the summation of the concentration detected in the aliphatic fraction and the concentration detected in the aromatic fraction.

Analytical Note: Due care must be exercised to assure that the peaks for naphthalene and n-dodecane in the aliphatic hydrocarbon fraction are adequately resolved to allow for an accurate determination of the naphthalene concentration in the LCS/LCSD pair.

Example Calculation of Naphthalene* % Breakthrough Calculation

Naphthalene in Aromatic Fraction (N aromatic) :::::::: 48 μg/L
Naphthalene in Aliphatic Fraction (N aliphatic) ::::::::: 1.5 μg/L
Total Naphthalene Concentration (N Tr)::::::::::::::::::: 49.5 μg/L
% Naphthalene Breakthrough = (Nal/NTr) X 100
% Naphthalene Breakthrough = 1.5/49.5 X 100

% Naphthalene Breakthrough = 3.0

* applies to 2-methylnaphthalene breakthrough calculation also.

10.7.3 At a minimum, with every batch of 20 samples or less the laboratory must extract and analyze the following quality control samples:

10.7.3.1 **Continuing Calibration Standard** - A mid-range continuing calibration standard, prepared from the same stock standard solution used to develop the calibration curve, must be analyzed prior to sample analysis to verify the calibration state of the instrument. For large analytical batches that contain more than 10 samples, the analysis of an additional mid-range continuing calibration standard is recommended after the analysis of the tenth sample. However, it should be noted that a mid-range continuing calibration standard is required after every 20 samples or every 24 hours (whichever comes first) and at the end of the analytical sequence. If the percent difference or percent drift of any analyte within the continuing calibration standard varies from the predicted response by more than 25%, a new five-point calibration must be performed for that analyte. Greater differences are permissible for n-nonane. If the percent difference or percent drift is greater than 30% for n-nonane, note the nonconformance in the narrative. For the closing continuing calibration standard (analyzed after every 20 samples, every 24 hours, or at end of analytical sequence), four compounds may exhibit percent differences or percent drifts greater than 25% but less than 40%.

10.7.3.2 **Laboratory Method Blank** - A water or soil Laboratory Method Blank is prepared by fortifying a reagent water or clean sand blank (for soils) with 1.0 mL of the surrogate spiking solution. Peaks must not be detected above the Reporting Limit within the
retention time window of any analyte of interest. The hydrocarbon ranges must not be
detected at a concentration greater than 10% of the most stringent MCP cleanup standard.
Peaks detected within the retention time window of any analyte or range of interest above a Reporting Limit must be noted on the data report form. Re-extraction of all associated
samples may be warranted.

10.7.3.3 **Laboratory Control Sample** - A Laboratory Control Sample is prepared by fortifying a reagent water or clean sand blank with 1.0 mL of

the matrix spiking solution. The spike recovery must be between 40% and 140%. Lower recoveries of n-nonane are permissible. If the recovery of n-nonane is <30%, note the nonconformance in the narrative. Re-extraction of all associated samples is required if criteria are not met.

10.7.3.4 **LCS Duplicate** - A Laboratory Control Sample Duplicate is prepared by fortifying a reagent water or clean sand blank with 1.0 mL of the matrix spiking solution The LCS Duplicate is separately prepared, processed and analyzed in the same manner as the LCS and is used as the data quality indicator of precision. The Analytical Batch Precision is determined from the Relative Percent Difference (RPD) of the concentrations (not recoveries) of LCS/LCSD pair. The RPD for individual Target PAH Analytes and aliphatic and aromatic hydrocarbon range concentrations (sum of the individual aliphatic or aromatic compounds within the specified range) must be ≤ 25%.

10.7.3.5 **Initial Calibration Verification** - An Initial Calibration Verification standard, prepared from a separate source standard than used for initial and continuing calibrations, must be analyzed prior to sample analysis if a separate source standard is not used for the LCS. The recoveries of all Target Analytes must be between 80-120%. A new five-point
calibration must be performed if criteria are not met.

10.7.3.6 **System Solvent Blank** - If baseline correction will be employed, a system solvent blank, air blank, and/or system run must be undertaken with every batch, and after the analysis of a sample that is suspected to be highly contaminated. In no case shall baseline correction be used if the instrument baseline drift is more than 25% greater than the average level established by these charts.

10.7.3.7 **Fractionation Check Standard** - A fractionation check solution is prepared containing 14 alkanes and 17 PAHs at a nominal concentration of 200 ng/ μl of each constituent. The Fractionation Check Solution must be used to evaluate the fractionation efficiency of each new lot of silica gel / cartridges and establish the optimum hexane volume required to efficiently elute aliphatic hydrocarbons while not allowing significant aromatic hydrocarbon breakthrough. For each analyte contained in the fractionation check solution, excluding n-nonane, the Percent Recovery

(see Appendix 5 of the referenced method), must be between 40 and 140%. A 30% Recovery is acceptable for n-nonane.
10.7.4 At the request of the data user, and in consideration of sample matricies and data quality objectives, matrix spikes and matrix duplicates may be analyzed with every batch of 20 samples or less per matrix.

10.7.4.1 **Matrix duplicate** - Matrix duplicates are prepared by analyzing one sample in duplicate. The purpose of the matrix duplicates is to determine the homogeneity of the sample matrix as well as analytical precision. The RPD of detected results in the matrix duplicate samples must not exceed 50% when the results are greater than 5x the reporting limit.

10.7.4.2 **Matrix Spike/Matrix Spike Duplicate** - The water or soil MS is prepared by fortifying an actual water or soil sample with 1.0 mL of the matrix spiking solution. The desired spiking level is 50% of the highest calibration standard. However, the total concentration in the MS (including the MS and native concentration in the unspiked sample) should not exceed 75% of the highest calibration standard in order for a proper evaluation to be performed. The purpose of the matrix spike is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate unspiked aliquot and the measured values in the matrix spike corrected for background concentrations. The corrected concentrations of each analyte within the matrix spiking solution must be within 40 - 140% of the true value. Lower recoveries of n-nonane are permissible, but must be noted in the narrative if <30%.

10.7.5 If any of the performance standards specified in Section 10.4 are not met, the cause of the nonconformance must be identified and corrected before any additional samples may be analyzed. Any samples run between the last QC samples that met the criteria and those that are fallen out must be re-extracted and/or re-analyzed. These QC samples include the opening continuing calibration standard, laboratory method blank, LCS, LCSD, and closing continuing calibration standard. If this is not possible, that data must be reported as suspect.

10.7.6 The analyte and hydrocarbon range Reporting Limits should be verified/re-established at least once per year, or upon a major change in system equipment or operations.

11.0 DATA PRODUCTION AND REPORTING

11.1 **Calibration**

Using the external standard calibration procedure (9.7.2) calibrate the GC as follows:

11.1.1 Calculate a CF or linear regression (LR) for each Target PAH Analyte that comprises the Aromatic Hydrocarbon standard. This step is not necessary if the Target or Diesel PAH Analytes will not be individually identified and quantitated by the EPH method (i.e., if unadjusted values only will be reported for the hydrocarbon ranges or TPH or if reporting concentrations of Target PAH Analytes via another method).

11.1.2 Calculate a CF for the surrogates OTP, COD and the Fractionation Surrogates.

11.1.3 Calculate a collective CF or LR for the total concentration of the C9 -C18 Aliphatic Hydrocarbons. Tabulate the summation of the peak areas of all component standards in that fraction (e.g., C9-C18 Aliphatics, 6 components) against the total concentration injected. Do not include any areal contribution of the internal standard, naphthalene, and 2-methylnaphthalene.

11.1.4 Calculate a CF or LR for naphthalene and 2-methylnaphthalene from the Aliphatic Hydrocarbon standard. Not required if the same instrument is calibrated, separately, for all aliphatic and aromatic compounds using the same internal standard and resolution of naphthalene from n-C12 is demonstrated..

11.1.5 Calculate a collective CF or LR for the total concentration of the C19 -C36 Aliphatic Hydrocarbons. Tabulate the summation of the peak areas of all component standards in that fraction (e.g., C19-C36 Aliphatics, 8 components) against the total concentration injected. Do not include the surrogate COD.

11.1.6 Calculate a collective CF or LR for the total concentration of the C11 -C22 Aromatic Hydrocarbons. Tabulate the summation of the peak areas of all component standards in that fraction (e.g., C11-C22 Aromatics, 17 components) against the total concentration injected. Do not include the surrogate OTP, 2-Bromonaphthalene, or 2-Fluorobiphenyl.

11.1.7 For TPH analyses, without fractionation, calculate a collective CF or LR. Tabulate the summation of the peak areas of all component standards in the aliphatic fraction (i.e., 14 components) against the total concentration injected. Do not include surrogates or naphthalene and 2-methylnaphthalene in the Aliphatic Hydrocarbon standard.

11.2 **Sample Analysis**

11.2.1 Aliphatic Fraction

11.2.1.1 Determine the total area count for all peaks eluting 0.1 minutes before the retention time (RT) for n-C9 and 0.01 minutes before the RTT for n-C19. It is not necessary to identify or quantitate individual aliphatic compounds within this range.

11.2.1.4 Determine the total area count for all peaks eluting 0.01 minutes before the RT for n-C19 and 0.1 minutes after the RT for n-C36. It is not necessary to identify or quantitate individual aliphatic compounds within this range.

11.2.1.4 Determine the peak area count for the surrogate standard (COD). Subtract this value from the collective area count value within the C19 through C36 aliphatic hydrocarbon range.

11.2.1.4 Using the equations contained in Section 9.9, calculate the collective concentrations of C9 through C18 Aliphatic Hydrocarbons, C19 through C36 Aliphatic Hydrocarbons, and the individual concentration of the surrogate COD.

11.2.2 Aromatic Fraction

11.2.2.1 Determine the total area count for all peaks eluting 0.1 minutes before the retention time (RT) for naphthalene and 0.1 minutes after the RT for benzo(g,h,i)perylene.

11.2.2.2 Determine the peak area count for the sample surrogate (OTP) and fractionation
surrogate(s). Subtract these values from the collective area count value.

11.2.2.3 Optionally, determine the peak area count for the Target or Diesel PAH Analytes.

11.2.2.4 Using the equations contained in Section 9.9, calculate the concentrations of Unadjusted C11 through C22 Aromatic Hydrocarbons, the surrogate standard (OTP), fractionation surrogate standard(s) and optionally, the Target or Diesel PAH Analytes.

11.2.3 Total Petroleum Hydrocarbons

11.2.3.1 Determine the total area count for all peaks eluting 0.1 minutes before the retention time
(Rt) for n-C9 and 0.1 minutes after the Rt for n-C36. It is not necessary to identify or
quantitate individual aliphatic compounds within this range.
11.2.3.2 Determine the peak area count for any surrogate and internal standards used. Subtract these values from the collective area count value.

11.2.3.3 Using the chemstation software, determine the concentration of Unadjusted TPH.

11.2.3.4 If the concentrations of the Target or Diesel PAH Analytes were determined using a GC/MS method, subtract the concentration of the Target or Diesel PAH Analytes from the concentration of unadjusted TPH and report concentration of resulting TPH. If the concentration of Target or Diesel PAH Analytes were not determined using a GC/MS
method, report a value for Unadjusted TPH, and indicate “Not Determined” for TPH.

11.2.4 Data Adjustments

11.2.4.1 By definition, the collective concentration of the aromatic fraction (and/or TPH) **excludes** the individual concentrations of the Target PAH Analytes. Accordingly, a data adjustment step is necessary to adjust the collective range concentration calculated in Sections 11.2.2.4 and 11.2.3.4, to eliminate “double counting” of analytes.

11.2.4.2 The necessary data adjustment step may be taken by the laboratory reporting the

range/TPH concentration data, or by the data user. The extent of data adjustments taken by the laboratory must be noted on the data report form.

11.2.4.3 Subtract the individual concentrations of the Target or Diesel PAH Analytes from the collective concentration of Unadjusted C11 through C22 Aromatic Hydrocarbons only if the concentrations of the Target or Diesel PAH Analytes are above the reporting limit. If the individual concentrations of Target PAH Analytes have been quantified using another method (e.g., by using an MS detector), note this on the data report form. It should be noted that the reported Target PAH Analyte results must be the results used to adjust the C11-C22 Aromatics results.

11.2.4.4 Subtract the individual concentrations of the Target or Diesel PAH Analytes from the collective concentration of Unadjusted TPH only if the concentrations of the Target or Diesel PAH Analytes were determined using a GC/MS method.

11.2.4.5 If the individual concentrations of Target PAH Analytes have not been quantitated, report a value for Unadjusted C11 through C22 Aromatic Hydrocarbons and/or Unadjusted TPH, and indicate “Not Determined” for C11 through C22 Aromatic Hydrocarbons and/or TPH.

11.2.4.6 For purposes of compliance with the reporting and cleanup standards specified in the Massachusetts Contingency Plan, the concentration of Unadjusted C11 through C22 Aromatic Hydrocarbons and/or Unadjusted TPH may be conservatively deemed to be equivalent to the concentration of C11 through C22 Aromatic Hydrocarbons and/or TPH.

11.2.5 Baseline Correction for Instrument Noise Level

11.2.5.1 EPH aliphatic and aromatic hydrocarbon range area data determined by the collective integration of all eluting peaks between the specified EPH range marker compounds (see Table 3) may be corrected by the manual or automatic subtraction of the baseline established by the injection of a System Solvent Blank. Correction in this manner is not recommended or preferred, but is permissible in cases where all reasonable steps have been taken to eliminate or minimize excessive baseline bias associated with analytical system noise.

11.2.5.2 The instrument baseline must be established by the direct injection of a system solvent blank. The injection of an air blank or activation of a temperature programmed
chromatographic run without the injection of any material should be used to verify that the system noise is not attributable to solvent contamination. All system operational elements and parameters must be identical to those of a typical sample run. If baseline correction is used, the baseline must be re-established for every analytical batch by the analysis of a System Solvent Blank. Baseline correction for EPH aliphatic and aromatic hydrocarbon area data may not be used for any sample for which the area count associated with the baseline correction is greater than 10% of the uncorrected area count for the sample's corresponding collective range.

11.2.6 Contamination of SPE Cartridges

11.2.6.1 Range integration areas may be affected by peaks identified during the injection of a Laboratory Method Blank, and determined to be attributable to the leaching of plasticizers or other contaminants from silica gel SPE cartridges. In general, this contamination affects the C11-C22 Aromatics. Blank correction is not permissible.

11.2.6.2 The laboratory must report the presence of this contamination in the associated range. Optionally, the laboratory may perform GC/MS analysis of the laboratory method blank extract to demonstrate that the contaminant in question is not a C11-C22 aromatic
compound. Analysis of only the method blank is acceptable as long as the associated
samples exhibit the same contaminant peak at the same retention time. If demonstrated not to be a C11-C22 aromatic compound, the contaminant does not need to be included in the calculation of the hydrocarbon range concentration. The laboratory must provide a
discussion in the case narrative if this approach is used.

11.3 **Data Reporting Content**

11.3.1 The data reported must reflect the unadjusted quantity of hydrocarbons in the fraction reporting (identifying the carbon range).

11.3.1.1 "Significant Modifications" to this method shall include, without limitation, all of the following:

11.3.1.1.1 The use of other than a silica-gel fractionation technique;

11.3.1.1.2 The use of solvents other than those recommended in this method.

11.3.1.1.3 The use of a detector other than a Flame Ionization Detector (FID) to quantitate range/TPH concentrations (See Notes 1 below);

11.3.1.1.4 The use of aliphatic or aromatic surrogate compounds with retention times not
within ± 2 minutes of the retention times of the recommended compounds or the use of inappropriate surrogates to represent the aliphatic and aromatic ranges;

NOTE
1: Use of a GC/MS detector operated in the Total Ion Current mode to quantify the EPH Method's aliphatic and aromatic hydrocarbon ranges is not considered a significant modification provided that (1) the sample extract has been fractionated; (2) the GC/MS system was also used to identify and quantify the Target PAH Analytes in the sample's aromatic fraction; and (3) the QC requirements and performance standards specified in Section 9.10 are satisfied.

11.3.2 In addition to sample results, if the client request a data package level III the EPH data report must contain the following items:

· Laboratory Method Blank Results
· Laboratory Control Sample Results
· LCS Duplicate Sample Results
· Matrix Spike Results
· Matrix Duplicate Results
· Fractionation Check Standard Results
· Surrogate Spike Recoveries (for all field samples and QC samples), including fractionation and extraction surrogates
· Percentage of total naphthalene and 2-methylnaphthalene concentrations detected in the aliphatic fractions of the LCS and LCS Duplicate (see Section 10.4.2)
· Results of re-analyses or dilutions must be reported

12.0 REPORTING LIMITS

The Reporting Limits (RLs) for Target PAH Analytes shall be based upon the concentration of the lowest calibration standard for the analyte of interest. The RL must be greater than or equal to the concentration of the lowest calibration standard.

Target PAH Analytes with calculated concentrations below the RL should be reported as < the specific Target Analyte's RL (i.e., < 2.0 ug/L).

If performing GC/MS target analysis only, calculated concentrations of Target PAH Analytes below the RL (lowest calibration standard) may be reported as a "J Value" (below MDL or equivalent). The RLs for hydrocarbon ranges shall be based upon the concentration of the lowest calibration standard for an individual analyte within the range of interest. The range RL will be set at 100x the concentration of the lowest calibration standard for the associated analyte. Calculated collective concentrations for EPH aliphatic and aromatic hydrocarbon ranges below the RL should be reported as < Range RL (i.e., < 100 ug/L). Based on the on-column concentration of 1 mg/L for the lowest calibration standard for all analytes, the following reporting limits would be generated for the hydrocarbon ranges:

Aqueous Samples: EPH Hydrocarbon range reporting limits would be equivalent to 100 μg/L based on the extraction of 1 liter of sample, a final fractionation extract volume of 2 mL, and a sample injection volume of 1 μL.

Soil/Sediment Samples: EPH Hydrocarbon range reporting limits would be equivalent to 20 mg/kg (dry weight basis) based on the extraction of 10 grams of soil, a final fractionation extract volume of 2 mL, and a sample injection volume of 1 μL.

13.0 METHOD PERFORMANCE

Single laboratory accuracy, precision and MDL data for method analytes are presently being generated in the method validation data can be provided along with chromatograms once completed, if requested (or can be provided in the data package (level III) reported with the samples. .

14.0 POLLUTION PREVENTION

14.1 Beckton provides satellite waste containers for disposal of solvent wastes and standards used in this method, the remaining water with salts used in the extraction are not hazardous to the environment and can be exposed as such.

14.3 EPA has published information about pollution prevention that is useful to know, consult "Less is Better: Laboratory Chemical Management for Waste Reduction", available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.

15.0 WASTE MANAGEMENT

15.1 Beckton's waste management practices are conducted consistent with all applicable rules and regulations, and that laboratories protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Also, Beckton discharge permit is monitored for compliance with all sewage discharge permits and regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult Mrs. Luisette Berastain (inhouse waste management atendant) and/or "The Waste Management Manual for Laboratory Personnel".

14.0 REFERENCES

1 MADEP and ABB Environmental Services, Inc., ″**METHOD FOR THE DETERMINATION OF EXTRACTABLE PETROLEUM HYDROCARBONS (EPH)**″, May, 2004 rev 1.1.

2 USEPA, ″Measurement of Petroleum Hydrocarbons: Report on Activities to Develop a Manual″ Prepared by Midwest Research Institute, Falls Church, VA, under EPA Contract #68-WO-0015, WA No. 4; submitted to USEPA Office of Underground Storage Tanks, Washington, DC; November 20, 1990.

3 USEPA ″SW-846 Test Methods for Evaluating Solid Waste″, 3rd Edition; Methods 3510C, 3520C, 3540C, 3541, 3545A, 3546, 3580A, 3630C, 8000B, 8100

4 USEPA Federal Register 40 CFR Part 136, Appendix B, ″Guidelines Establishing Test Procedures for the Analysis of Pollutants″, July 1992.

5 Wisconsin Department of Natural Resources, ″Modified DRO - Method for Determining Diesel Range Organics″, PUBL-SW-141, 1992

6 USEPA, "Guidance on Evaluation, Resolution, and Documentation of Analytical Problems Associated with Compliance Monitoring", EPA 821-B-93-001; U.S. Government Printing Office, Washington D.C., June, 1993

7 Massachusetts DEP, “Report on the Results of the Fall 1997 VPH/EPH Round Robin Testing Program”, December, 1997
8 EPA UST Workgroup, Draft ″Method for Determination of Diesel Range Organics″, November, 1990
9 ASTM 1990. Standard Method for Laboratory Determination of Water (Moisture) Content of Soil and Rock, *Annual Book of ASTM Standards*, D 2216-90 (revision of 2216-63, 2216-80).
10 USEPA Federal Register 40 CFR Part 136, Appendix B, ″Guidelines Establishing Test Procedures for the Analysis of Pollutants″, July 1992.
11 Wisconsin Department of Natural Resources, ″Modified DRO - Method for Determining Diesel Range Organics″, PUBL-SW-141, 1992
12 USEPA, “Guidance on Evaluation, Resolution, and Documentation of Analytical Problems Associated with Compliance Monitoring”, EPA 821-B-93-001; U.S. Government Printing Office, Washington D.C., June, 1993
13 Massachusetts DEP, “Report on the Results of the Fall 1997 VPH/EPH Round Robin Testing Program”, December, 1997
14 EPA UST Workgroup, Draft ″Method for Determination of Diesel Range Organics″, November, 1990
15 ASTM 1990. Standard Method for Laboratory Determination of Water (Moisture) Content of Soil and Rock, *Annual Book of ASTM Standards*, D 2216-90 (revision of 2216-63, 2216-80).

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